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# Revisiting the Use of 2,6-Dimethylpyridine Adsorption as a Probe for the Acidic Properties of Metal Oxides

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To check if the adsorption/desorption of 2,6-dimethylpyridine (2,6-DMP) is a suitable probe for the surface acidity of oxides, and to assign a band of controversial interpretation often observed upon 2,6-DMP adsorption, the ambient temperature uptake of 2,6-DMP on several oxidic systems was carried out. SiO<sub>2</sub> was observed to yield a plain H-bonding interaction, characterized by an 8a band of adsorbed 2,6-DMP that is typical of silanols. Several (spinel) transition aluminas and the corundum  $\alpha$ -alumina phase were examined and allowed to test the suitability of 2,6-DMP in distinguishing different types of surface Lewis acidity. Sulfated alumina and a  $\beta$ -zeolite in its H-form were used to check the sensitivity of 2,6-DMP uptake toward either induced or intrinsic Brønsted acidity and the possibility of observing (weak) Lewis-coordinated 2,6-DMP also in the presence of (strong) Brønsted-bound 2,6-DMP.

## Introduction

IR spectroscopy of the adsorption/desorption of basic molecules, like for instance ammonia or pyridine and its derivatives, is an often used method to characterize the surface acidity of solids, in that this method is considered to be able to titrate concentration and strength of surface acid sites.

The adsorption of pyridine (py) as a tool to test the acidity of oxidic systems has been proposed long ago.<sup>1</sup> This molecule can distinguish between Lewis and Brønsted acidity, giving rise to specific IR absorption bands.<sup>1,2</sup> Among the various bands, one located at  $\sim 1450\text{ cm}^{-1}$  (due to Lewis-coordinated py) and one located at  $\sim 1540\text{ cm}^{-1}$  (due to Brønsted-bound py) are both associated with the 19b ring mode of py and are usually considered as analytical of the interaction of py with coordinatively unsaturated (cus) Me<sup>n+</sup> cations and with protonic sites,<sup>3</sup> respectively.

If py contains substituent groups in the 2- and 6-position, as in the case of lutidine (i.e., 2,6-dimethylpyridine, hereafter referred to as 2,6-DMP), the formation of coordinative chemisorption bonds is expected to be sterically hindered.

In the literature, many works are present dealing with the adsorption of sterically hindered pyridines onto oxidic systems.<sup>4–13</sup> Some authors<sup>4–6</sup> have suggested, on the basis of 2,6-DMP adsorption/desorption measurements on dif-

ferent oxidic systems, that this base plays the role of specific proton probe, also in the presence of surface Lewis acid sites. In fact, they report that this base interacts first with Brønsted acid sites and subsequently and only under high adsorptive pressures with Lewis sites. Moreover, some authors claim that when 2,6-DMP is adsorbed, they cannot distinguish among Lewis acid sites of different acidic strengths (e.g., see refs 9 and 13), and most authors report that the Lewis coordinative interaction of 2,6-DMP is so weak (due to steric hindrance) that is never realized for adsorption/desorption at  $T \geq 423\text{ K}$ .

Sometimes, the adsorption of 2,6-DMP on oxidic systems has been reported to give rise to a band located at  $\sim 1618\text{ cm}^{-1}$ ,<sup>7,8</sup> and this absorption seems to be never present in zeolitic systems.<sup>6,9</sup> The assignment of this peak is still a controversial matter,<sup>7–12</sup> as some authors assigned it to a very strong Lewis-coordinated species, whereas other authors ascribed it to a very weak Brønsted (protonic) interaction.

The aim of this work is 2-fold: (i) to prove that 2,6-DMP is a valid probe for Lewis surface acidity, as well as other basic molecules,<sup>11,12</sup> even if steric hindrance yields weaker Lewis complexes than in the case of other basic adsorbates; (ii) to assign the controversial band, located at  $\sim 1618\text{ cm}^{-1}$ , on the basis of 2,6-DMP adsorption/desorption experiments carried out onto different oxidic systems and in different hydration/dehydration conditions.

## Experimental Section

**Materials.** As a SiO<sub>2</sub> sample, we used Aerosil 200, which is a commercial product supplied by Degussa (Frankfurt aM, Germany). The material is amorphous and nonporous, and its BET surface area is  $200\text{ m}^2\text{ g}^{-1}$ .

A sample of pure  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was prepared by calcination at 773 K of pure bohemite ( $\gamma$ -AlOOH), prepared and supplied by Centro Ricerche Fiat (Orbassano, Italy). Starting from this  $\gamma$ -alumina, a subsequent calcination at either 1273 or 1473 K allowed us to obtain either the  $\delta,\theta$ -Al<sub>2</sub>O<sub>3</sub> modification or the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> modification, respectively. The phase composition of the three alumina samples was checked by the XRD technique, and the diffractograms were found to be consistent with those reported in the literature (e.g., see ref 14). The mesoporous nature of the two transition aluminas and the nonporous nature of the corundum alumina phase were all consistent with those first described by Lippens et al.<sup>14</sup> The BET surface area was found to be  $200\text{ m}^2\text{ g}^{-1}$  ( $\gamma$ -Al<sub>2</sub>O<sub>3</sub>),  $120\text{ m}^2\text{ g}^{-1}$  ( $\delta,\theta$ -Al<sub>2</sub>O<sub>3</sub>), and  $4\text{ m}^2\text{ g}^{-1}$  ( $\alpha$ -Al<sub>2</sub>O<sub>3</sub>).

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A sample of sulfated alumina, hereafter referred to as  $\gamma$ -AS, was prepared by sulfating with 0.1 N  $\text{H}_2\text{SO}_4$  the above-mentioned  $\gamma$ - $\text{Al}_2\text{O}_3$  preparation, so as to obtain a surface sulfates concentration of  $\sim 3 \text{ SO}_4^{2-}/\text{nm}^2$ . Both crystal phase and BET surface area of the  $\gamma$ - $\text{Al}_2\text{O}_3$  sample were found not to be significantly influenced by the sulfation process.

A sample of  $\beta$ -zeolite in its H-form (hereafter referred to as H- $\beta$ ) was kindly supplied by Dr. S. Bordiga (University of Turin, Turin, Italy). The material, usually employed for the alkylation of aromatics, was of industrial provenance<sup>15</sup> and was characterized by a Si/Al ratio of 14.5.

**Techniques.** Fourier transform infrared (FTIR) spectra were obtained at  $2 \text{ cm}^{-1}$  resolution with a Bruker IFS113v spectrophotometer connected to a glass vacuum line (residual pressure  $< 10^{-5}$  Torr) that allows to perform strictly in situ adsorption/desorption runs. The samples were examined in the form of either self-supporting pellets ( $\sim 15 \text{ mg cm}^{-2}$ ) or thin layer depositions ( $\sim 10 \text{ mg cm}^{-2}$ ) on Si wafers.

Prior to adsorption/desorption experiments, all samples were activated in situ at the selected temperatures in homemade quartz IR cell (equipped with KBr windows) connected to the vacuum line.

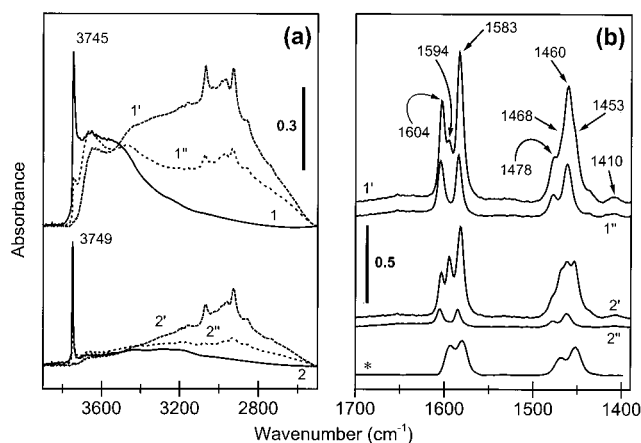
2,6-DMP adsorption/desorption tests were carried out as follows: (i) A relatively large amount of base ( $\sim 4$  Torr) was first allowed on the samples and left in contact at beam temperature (BT;  $\sim 333$ – $343 \text{ K}$ ) for 2 min. (ii) The excess 2,6-DMP was then evacuated at BT for increasing times in the 1–15 min range. (iii) A desorption of the strongly bonded base fraction was eventually carried out at  $423 \text{ K}$ .

## Results and Discussion

**2,6-DMP Adsorption onto  $\text{SiO}_2$ .** Silica was activated in vacuo at two different temperatures ( $473$  and  $1073 \text{ K}$ ), to obtain different surface dehydration levels. After vacuum activation at  $473 \text{ K}$ , no undissociated adsorbed water is present anymore, but the surface of Aerosil 200 is still largely hydrated, as the dehydroxylation process of nonporous silicas is completed only for much higher activation temperatures. In fact, the  $3900$ – $2500 \text{ cm}^{-1}$  spectral range (the  $\nu_{\text{OH}}$  spectral range; see curve 1 in Figure 1a) still contains at least two contributions: (i) at high frequency ( $\sim 3745 \text{ cm}^{-1}$ ), the well-known  $\nu_{\text{OH}}$  stretching mode of terminal silanols free from H-bonding interactions; (ii) at lower frequency ( $3650$ – $3100 \text{ cm}^{-1}$ ), a broad and unresolved envelope due to the  $\nu_{\text{OH}}$  stretching modes of OH groups still interacting by H-bonding. When the activation temperature is as high as  $\sim 1073 \text{ K}$ , the broad tailing at low  $\nu$  totally disappears, and the high- $\nu$  spectral range (see curve 2 in Figure 1a) presents only a sharp peak located at  $\sim 3750 \text{ cm}^{-1}$ , due to residual free OH groups.

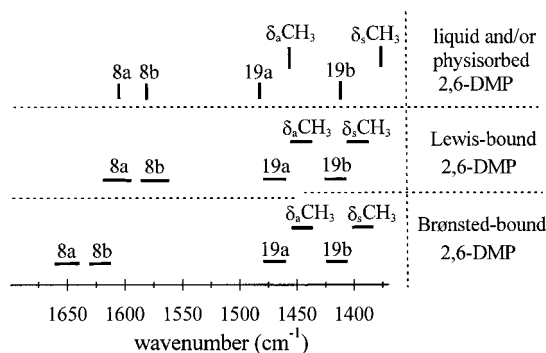
After adsorption of 2,6-DMP onto silica activated at  $423 \text{ K}$ , in the  $\nu_{\text{OH}}$  spectral range ( $3900$ – $2500 \text{ cm}^{-1}$ ; see curve 1' in Figure 1a) several spectral changes are observed: (i) The  $\nu_{\text{OH}}$  stretching mode of free silanols ( $\sim 3745 \text{ cm}^{-1}$ ) disappears. (ii) The broad envelope at  $\sim 3650$ – $3100 \text{ cm}^{-1}$ , ascribed to the H-bonding interactions among surface OH groups, shows a decreased intensity. (iii) A strong and broad band envelope forms at  $\nu < 3200 \text{ cm}^{-1}$ . All these spectral features clearly indicate that 2,6-DMP uptake involved in H-bonding of medium strength ( $\Delta\nu_{\text{OH}} \approx -700 \text{ cm}^{-1}$ ) all of the free surface OH species and an appreciable fraction of the surface OH species still involved in H-bonding.

Upon evacuation at BT (spectrum 1'' of Figure 1a), the perturbation caused in the  $\nu_{\text{OH}}$  spectrum by 2,6-DMP



**Figure 1.** (a) OH spectral pattern (in the  $3900$ – $2500 \text{ cm}^{-1}$  range) of an Aerosil-200 sample activated in vacuo at  $473 \text{ K}$  (spectral set 1) and at  $1073 \text{ K}$  (spectral set 2). (b) IR spectra in the analytical range  $1700$ – $1400 \text{ cm}^{-1}$  (8a, 8b, 19a, 19b, and  $\delta_{\text{CH}_3}$  modes) of 2,6-DMP adsorbed onto an Aerosil-200 sample activated in vacuo at  $473 \text{ K}$  (spectral set 1) and at  $1073 \text{ K}$  (spectral set 2). In both sections, the primed numbers refer to the adsorption of a large dose of 2,6-DMP ( $\sim 4$  Torr) and the double-primed numbers refer to the evacuation of 2,6-DMP at beam temperature (BT) for 15 min. The reference spectrum, marked with an asterisk, corresponds to liquid 2,6-DMP.

**Chart 1. Spectral Location of Mid-IR Vibrational Modes of Free and Adsorbed 2,6-DMP**

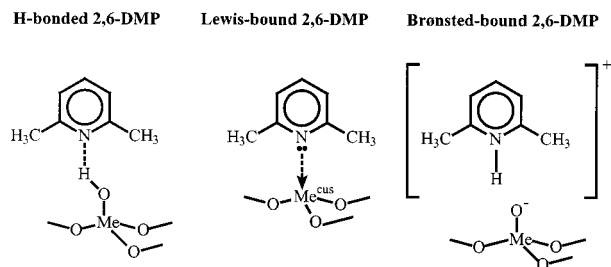


adsorption is only partly eliminated, whereas after evacuation at  $423 \text{ K}$  the original  $\nu_{\text{OH}}$  spectrum is fully recovered.

As for the analytical mid-IR spectral range ( $1700$ – $1400 \text{ cm}^{-1}$ ), 2,6-DMP species usually present two groups of bands. Figure 1b shows a series of spectra obtained after adsorption/desorption of 2,6-DMP onto the differently activated silica specimens. The spectral segments considered in the following comprise both the analytical range of ring stretching modes 19a, 19b and 8a, 8b and that of the two  $\delta_{\text{CH}_3}$  deformation modes, as reported in Chart 1. (a) When the surface of  $\text{SiO}_2$  is only partially dehydrated, in the presence of 2,6-DMP vapors many bands form: among them, the bands ascribable to a liquid-like (physisorbed) 2,6-DMP species are observed, lying at  $\sim 1594$ ,  $\sim 1583$ ,  $\sim 1468$  (shoulder),  $\sim 1453$  (shoulder), and  $\sim 1410 \text{ cm}^{-1}$  (very weak); the first four bands correspond to the only bands observable in the reference spectrum (marked with an asterisk in Figure 1b) relative to liquid 2,6-DMP. It is worthwhile noting that the peaks located at lower frequencies ( $\sim 1400$ – $1480 \text{ cm}^{-1}$ ) are little useful in analytical terms, because they undergo little spectral (upward) changes upon adsorption. On the other hand, the second group of bands ( $\sim 1580$ – $1605 \text{ cm}^{-1}$ ) gives more information: the strong band at  $1583 \text{ cm}^{-1}$  (the 8b mode) is due to both physisorbed (liquid-like) species and H-bonding

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**Chart 2. Graphical Representation of the Possible 2,6-DMP/Surface Interactions**

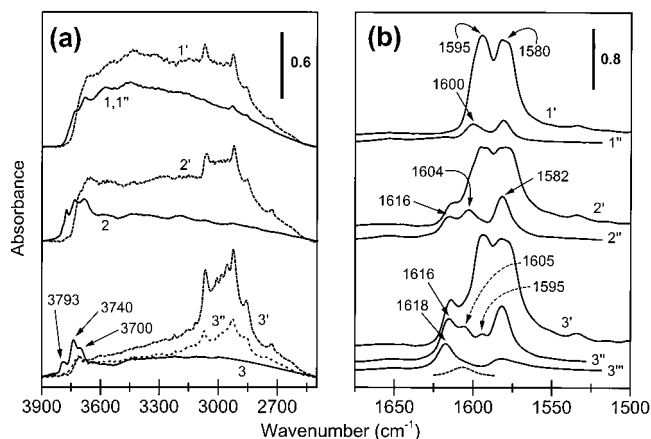
interacting 2,6-DMP molecules (Chart 2). The  $\sim 1594\text{ cm}^{-1}$  band is due to the 8a mode of physisorbed molecules, whereas the peak located at  $1604\text{ cm}^{-1}$  can be assigned to the 8a mode of a stronger form of adsorbed 2,6-DMP, i.e., to 2,6-DMP interacting by H-bonding with surface silanols.

After evacuation at BT (see curve 1'' in Figure 1b), bands remain, though with a drastically decreased intensity, at  $\sim 1604$ ,  $\sim 1478$ ,  $\sim 1460$ , and  $\sim 1410\text{ cm}^{-1}$  (very weak), together with a residual component at  $1580\text{ cm}^{-1}$ , due to the 8b mode common to all adsorbed 2,6-DMP species. On the basis of the spectral behavior, these bands can be confirmed to be ascribable to the 8a, 8b, 19a, 19b, and  $\delta_{\text{CH}_3}$  modes of 2,6-DMP interacting by H-bonding with surface OH groups still abundantly present on the surface. In particular, the large upward shift undergone by the 8a mode of H-bonded 2,6-DMP ( $\sim 1604\text{ cm}^{-1}$  is a frequency often observed for 2,6-DMP coordinated to Lewis acid sites) is not unexpected, as, also with other molecules (e.g., acetonitrile<sup>16</sup>), surface silanols were observed to yield, by H-bonding, large spectral shifts comparable to the shifts normally observed with Lewis acid–base interactions of medium strength.

(b) When silica is activated at high temperatures ( $\sim 1073\text{ K}$ ; see curve 2' in Figure 1b), in the  $1650\text{--}1400\text{ cm}^{-1}$  spectral range no new bands are added to the above-mentioned ones. The only difference is that the overall 2,6-DMP uptake is somewhat decreased, and there is a largely enhanced ratio between physisorbed and H-bonded species, as a consequence of a far decreased surface concentration of OH species capable of H-bonding the adsorbate. In the  $\nu_{\text{OH}}$  spectral range, the spectral changes ( $\Delta\nu_{\text{OH}} \approx -700\text{ cm}^{-1}$ ) confirm the profile already evidenced for the sample activated at lower  $T$  (see curves 2 and 2' in Figure 1a). Upon evacuation at BT, a much larger fraction of H-bonded 2,6-DMP is desorbed (with respect to the sample activated at low temperature), and when 2,6-DMP is desorbed at  $423\text{ K}$ , all the spectral features due to adsorbed species disappear and the background spectrum recovers the starting shape in all spectral ranges examined.

**2,6-DMP Adsorption onto Aluminas ( $\gamma$ -,  $\delta$ -,  $\theta$ -, and  $\alpha$ -Phases).** (a)  $\gamma$ -Alumina.  $\gamma$ -Alumina was chosen as a test adsorbent because of its large use in catalytic applications and for its strong Lewis acidity (see, for instance, ref 17 and references therein). Alumina was vacuum activated at three increasing temperatures ( $473$ ,  $773$ , and  $1023\text{ K}$ , respectively), to achieve a progressive surface dehydration, and thus create at the surface larger and larger concentrations of cus cationic sites, acting as surface Lewis acid sites.

When the sample is activated at  $473\text{ K}$ , it is freed from all undissociated (coordinated) water, but it is only very



**Figure 2.** (a) OH spectral pattern (in the  $3900\text{--}2500\text{ cm}^{-1}$  range) of a  $\gamma$ -alumina sample activated in vacuo at  $473$ ,  $773$ , and  $1023\text{ K}$  (spectral sets 1–3, respectively). (b) Spectral features in the analytical range of the 8a, 8b modes ( $1700\text{--}1500\text{ cm}^{-1}$ ) of 2,6-DMP adsorbed onto  $\gamma$ -alumina activated in vacuo at  $473$ ,  $773$ , and  $1023\text{ K}$  (spectral sets 1–3, respectively). In both sections, the curves marked with the prime symbol refer to 2,6-DMP adsorption at BT and under a relatively high pressure ( $\sim 4\text{ Torr}$ ), whereas the curves marked with the double- and triple-primed symbols refer to 2,6-DMP desorption at BT and at  $423\text{ K}$ , respectively.

slightly dehydroxylated (if at all). This is clearly observable in the  $\nu_{\text{OH}}$  stretching region (see Figure 2a, curve 1), where a broad and unresolved band envelope, due to H-bonded OH species, is still present at  $\nu < 3700\text{ cm}^{-1}$ . Only two shallow peaks lying at high frequency are ascribable to OH groups already free from H-bonding. Activation at higher temperatures (see curves 2 and 3 in Figure 2a) produces a more and more dehydrated surface, and the  $\nu_{\text{OH}}$  spectral pattern acquires a well-known five-band profile,<sup>17–19</sup> whose shape and overall intensity is largely determined by the activation temperature reached.

Figure 2b shows the IR spectra in the 8a, 8b spectral range of 2,6-DMP adsorbed onto  $\gamma$ -alumina activated at the three different temperatures mentioned above. Only the higher- $\nu$  subrange, due to 8a, 8b modes, is here examined, because the presence on alumina of several 2,6-DMP adsorbed species renders the band's envelope at  $\nu < 1550\text{ cm}^{-1}$  broad and very poorly resolved, so that its analytical use is virtually null.

When the activation is carried out at the lowest temperature (see the spectral set 1 in Figure 2b), a two-band profile is observed centered at  $\sim 1595$  and  $\sim 1580\text{ cm}^{-1}$ , mostly due to a liquid-like 2,6-DMP species. But the broad and asymmetric band at  $\sim 1595\text{ cm}^{-1}$  is most likely made up of several contributions: (i) One is certainly due to a fast reversible weak physisorbed species (i.e., the mentioned liquid-like species). (ii) A second nonresolved component could be due to 2,6-DMP interacting by H-bonding with surface OH species, but a specific 8a mode could not be singled out. Still, the dramatic spectral changes observed in the  $\nu_{\text{OH}}$  spectral region (see Figure 2a) indicate that surface OH species are indeed perturbed by H-bonding upon 2,6-DMP adsorption. (iii) Another component could be ascribable to 2,6-DMP molecules interacting with weak Lewis acid centers. In fact, when the excess 2,6-DMP is outgassed at BT, the global intensity of the 8a, 8b mode envelope decreases dramatically, while the  $\nu_{\text{OH}}$  profile is fully recovered, and curve 1'' in Figure

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2b indicates that an 8a peak remains, centered at  $\sim 1600\text{ cm}^{-1}$ , together with a residual 8b component at  $1581\text{ cm}^{-1}$ . It is recalled that, upon activation at 473 K, alumina is freed from coordinated undissociated water, and this ligand removal leaves behind the first (weak) Lewis sites, as it has been evaluated by the adsorption of  $\text{CO}_2$  (at room temperature) or of CO at low temperature.<sup>17</sup> The band at  $\sim 1600\text{ cm}^{-1}$  is thus assignable to the 8a mode of (a first family of) weak Lewis acid sites.

A more complex situation is observed when  $\gamma$ -alumina is vacuum activated at 773 and 1023 K (see, in Figure 2b, the spectral sets 2 and 3, respectively). The dehydration process has proceeded, and in both cases the adsorption of 2,6-DMP produces, in the  $1700\text{--}1500\text{ cm}^{-1}$  range, a complex band envelope made up of, at least, three broad components (centered at  $\sim 1575$ ,  $\sim 1590$ , and  $\sim 1610\text{ cm}^{-1}$ , respectively). If the excess 2,6-DMP is pumped off, the labile (physisorbed and H-bonded) species are removed and in the analytical spectral region three peaks (activation at 773 K, curve 2'' of Figure 2b) and four peaks (activation at 1023 K, curve 3'' of Figure 2b) remain. The first one, located at  $\sim 1582\text{ cm}^{-1}$ , is assigned to the overlapping 8b modes of all 2,6-DMP species, whose 8a modes lie at higher wavenumbers.<sup>6</sup> As in the case of pyridine adsorption, also for 2,6-DMP the rule is that the higher is the 8a mode of the coordinated base, the stronger is the interaction between the coordinated base and the adsorption site. For this reason, the proposed assignment for the (up to) three 8a mode bands observed in Figure 2b is as follows:

(i) The band located at the highest  $\nu$  ( $\sim 1616\text{ cm}^{-1}$ ), and thus corresponding to 2,6-DMP complexes formed at sites characterized by the highest Lewis acidity, can be ascribed to 2,6-DMP molecules interacting with *cus*  $\text{Al}^{3+}$  cations possessing an incomplete tetrahedral coordination. It is known that these sites are the most important component of the strong Lewis acidity for which transition aluminas are appreciated for many catalytic applications. (It is recalled that, on the highly acidic low-temperature transition aluminas ( $\gamma$ - and  $\eta$ - $\text{Al}_2\text{O}_3$ ), py yields with *cus*  $\text{Al}^{3+}$  sites strong complexes whose 8a mode is observed at frequencies as high as  $\sim 1622\text{ cm}^{-1}$ .)

(ii) As for the 8a band located at  $\sim 1603\text{--}1606\text{ cm}^{-1}$ , it can be ascribed to 2,6-DMP complexes formed at coordinative vacancies bridging between  $\text{Al}^{\text{IV}}$  and  $\text{Al}^{\text{VI}}$  surface cationic centers. (It is recalled that, on low-temperature transition aluminas ( $\gamma$ - and  $\eta$ - $\text{Al}_2\text{O}_3$ ), py yields with these coordinative vacancies complexes whose 8a mode lies at  $\sim 1614\text{ cm}^{-1}$ .)

(iii) Finally, the 8a band located at  $\sim 1595\text{ cm}^{-1}$  (some of which remains on  $\gamma$ - $\text{Al}_2\text{O}_3$  treated at 1073 K also after evacuation at BT) may have a double nature, as in this spectral position two different contributions are possible. One contribution can derive from the H-bonding interaction of 2,6-DMP with some surface OH species, whereas the other one can be due to the interaction of 2,6-DMP with Lewis acid sites weaker than the ones already mentioned, i.e. with coordinative vacancies on octahedrally coordinated ( $\text{Al}^{\text{VI}}$ ) sites. Both of these assignments imply some surprising aspects: it is surprising that some H-bonded 2,6-DMP species remain, after evacuation at BT, only on the sample activated at the highest temperature (on which all five different OH species are still present, but there should be the lowest overall amount of OH species), and it is surprising that (some of) the base Lewis coordinated to the weakest acid sites remains after evacuation at BT only on the sample activated at the highest temperature, on which the surface concentration of strong Lewis acid sites is maximum. In fact, on

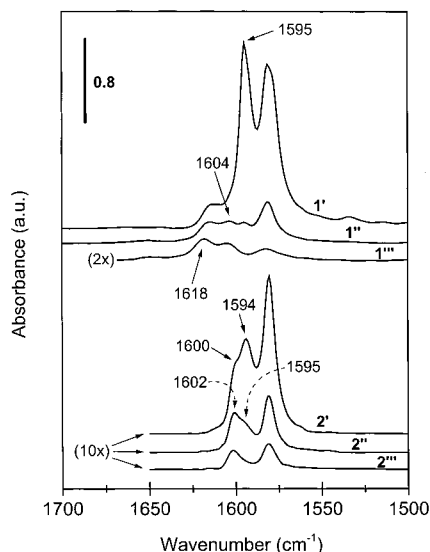
insulating systems, most frequently the coordination to weak charge-withdrawing sites is observable only in the absence of complexes formed at stronger charge-withdrawing sites. Still, we favor the latter assignment, as on all other systems examined (but silica) the elimination of H-bonded 2,6-DMP is observed to be complete upon evacuation at BT.

After a vacuum desorption treatment at 423 K (see, for instance, the spectral set 3 of Figure 2b, relative to  $\gamma$ - $\text{Al}_2\text{O}_3$  activated at 1073 K), the overall bands intensity decreases but is not eliminated. The high- $\nu$  8a mode (now centered at  $\sim 1618\text{ cm}^{-1}$ ) remains with almost unchanged intensity, whereas only some 15% of the 8a mode at  $\sim 1606\text{ cm}^{-1}$  remains, as indicated in the figure by the dotted-line-resolved component. (Obviously, also a contribution of the unresolved 8b mode remains at  $\sim 1584\text{ cm}^{-1}$ .) This indicates that an adsorption/desorption temperature of  $\sim 423\text{ K}$  is not sufficient to prevent/eliminate the coordination of 2,6-DMP onto/from strong Lewis sites of alumina, i.e., on coordinative vacancies involving  $\text{Al}^{\text{IV}}$  centers.

The data for 2,6-DMP adsorption/desorption on  $\gamma$ -alumina so indicate that, unlike what previously reported,<sup>13</sup> at temperatures as high as  $\sim 423\text{ K}$  this base still probes selectively the strongest Lewis acid sites and that, unlike what reported by other authors,<sup>10</sup> this base can distinguish Lewis acid sites of different strength, much as other bases do. Moreover, the present data indicate that, at least on  $\gamma$ - $\text{Al}_2\text{O}_3$ , the controversial 8a band at  $\sim 1618\text{ cm}^{-1}$  is ascribable to a strong Lewis interaction (actually, the strongest one) and not to a weak Brønsted interaction that, on pure alumina, is not present at all.

(b)  $\delta$ ,  $\theta$ - and  $\alpha$ -Aluminas. To confirm the above hypothesis and spectral assignments, we performed some adsorption/desorption experiments of 2,6-DMP onto  $\delta$ ,  $\theta$ - and  $\alpha$ -alumina specimens activated at 1073 K, i.e., in highly dehydrated conditions. The interest in these alumina modifications consists of the following facts: (i)  $\delta$ ,  $\theta$ - $\text{Al}_2\text{O}_3$  (one of the so-called high-temperature transition aluminas) still possesses a defective spinel structure but should possess a lower surface concentration of highly defective  $\text{Al}^{3+}$  centers with an incomplete tetrahedral coordination.<sup>17</sup> This system is thus suitable for confirming the ability of 2,6-DMP to differentiate among Lewis sites of different strength. (It is recalled that, using a  $\delta$ ,  $\theta$ - $\text{Al}_2\text{O}_3$  modification, other authors<sup>13</sup> observed only one Lewis coordinated species and, thus, concluded that 2,6-DMP is not a suitable probe for the Lewis acidity of metal oxides.) (ii)  $\alpha$ - $\text{Al}_2\text{O}_3$  has a different crystal structure (corundum), and at least in the bulk (i.e., in regular conditions), should possess  $\text{Al}^{3+}$  ions only in the octahedral coordination. Also this system is thus suitable for confirming the ability of 2,6-DMP to differentiate among Lewis sites of different strength.

(i) The adsorption/desorption of 2,6-DMP onto a highly dehydrated  $\delta$ ,  $\theta$ - $\text{Al}_2\text{O}_3$  system (see spectral set 1 in Figure 3) brings about the formation of the same 8a, 8b bands described above for the  $\gamma$ -alumina specimen vacuum activated at the same high temperature, but the intensity ratios are here quite different. In particular, if we compare the spectra obtained on  $\gamma$ - $\text{Al}_2\text{O}_3$  and on  $\delta$ ,  $\theta$ - $\text{Al}_2\text{O}_3$  after 2,6-DMP evacuation at BT (curve 3'' in Figure 2b and curve 1'' in Figure 3, respectively), it is quite evident that the amount of irreversible adsorbate is small in both cases (as witnessed by the weak 8b mode remaining at  $\sim 1580\text{ cm}^{-1}$  after evacuation), but on the  $\delta$ ,  $\theta$ - $\text{Al}_2\text{O}_3$  system there is an appreciably decreased amount of the strongest species ( $\sim 1616\text{ cm}^{-1}$ , assigned to *cus* tetrahedral Al sites) and an increased relative amount of the other two species ( $\sim 1604\text{ cm}^{-1}$ , assigned to coordinative vacancies bridging between



**Figure 3.** Analytical spectral range of the 8a, 8b modes (1700–1500  $\text{cm}^{-1}$ ) of 2,6-DMP adsorbed onto different alumina samples activated in vacuo at 1023 K (set 1,  $\delta,\theta$ -alumina; set 2,  $\alpha$ -alumina). The curves marked with the prime symbol refer to 2,6-DMP adsorption at BT and under a relatively high pressure ( $\sim 4$  Torr), whereas the curves marked with the double- and triple-primed symbols refer to 2,6-DMP desorption at BT and at 423 K, respectively. For the sake of clarity, some of the spectra were ordinate-magnified, as reported on the curves.

tetrahedral and octahedral  $\text{Al}^{3+}$  ions, and  $\sim 1594 \text{ cm}^{-1}$ , (tentatively) assigned to cus  $\text{Al}^{3+}$  ions with octahedral coordination). Also after 2,6-DMP evacuation at 423 K (curve 3''' in Figure 2b and curve 1''' in Figure 3), the residual 8a, 8b bands confirm that, at this temperature, the strongest Lewis acid sites can still adsorb the base, and the relative intensity of the two 8a modes (now at  $\sim 1618$  and  $\sim 1604 \text{ cm}^{-1}$ , respectively) confirms that, on  $\delta,\theta\text{-Al}_2\text{O}_3$ , the surface concentration of strongly defective  $\text{Al}^{\text{IV}}$  cus sites is lower than in the case of  $\gamma\text{-Al}_2\text{O}_3$ . The fact that, on a similar  $\delta,\theta\text{-Al}_2\text{O}_3$  system, other authors<sup>13</sup> did not observe the multiplicity of species here observed is (at least partly) due to the fact that, in that case, the activation was carried out at a much lower temperature, so that most of the more energetic Lewis acid sites were still missing (i.e., the surface of the transition alumina was still in a highly hydrated form).

(ii) The adsorption/desorption of 2,6-DMP onto an  $\alpha\text{-Al}_2\text{O}_3$  system activated at 1073 K (at this temperature,  $\alpha\text{-Al}_2\text{O}_3$  is virtually fully dehydrated) leads to the formation of a lower number of spectral components (see set 2 in Figure 3). This is better seen in the spectral pattern 2'', relative to the BT evacuation of the excess 2,6-DMP and removal of all weakly adsorbed species. Besides the band located at  $\sim 1580 \text{ cm}^{-1}$  (the 8b mode of all 2,6-DMP adsorbed species), the 8a spectral range presents two components of odd intensity: one (stronger) component is centered at  $\sim 1602 \text{ cm}^{-1}$ , and a second one is present as an evident shoulder at  $\sim 1595 \text{ cm}^{-1}$ . On the basis of the spectral position, the former band can be ascribed to the interaction of 2,6-DMP with quasi-tetrahedral  $\text{Al}^{3+}$  sites, sharing a coordination vacancy with an octahedral  $\text{Al}^{3+}$  ion, and the latter band to the interaction of 2,6-DMP with purely octahedral  $\text{Al}^{3+}$  cus sites. (In the same spectral position there might be also a contribution from H-bonded 2,6-DMP species, but this possibility is low in that, as reported above,  $\alpha\text{-Al}_2\text{O}_3$  activated at 1023 K is virtually fully dehydroxylated.) The band due to 2,6-DMP complexes formed at cus octahedral sites should, on  $\alpha\text{-Al}_2\text{O}_3$ , be the sole coordinated species formed, as the corundum structure

implies for cationic species the sole octahedral coordination. As a matter of fact, the 8a band at  $\sim 1595 \text{ cm}^{-1}$  was definitely much stronger under a high 2,6-DMP pressure (see curve 2') and was then drastically reduced during the BT evacuation, but it was not the only Lewis-coordinated species present. The presence at the surface of the corundum  $\alpha\text{-Al}_2\text{O}_3$  phase of defective quasi-tetrahedral  $\text{Al}^{3+}$  sites is not unexpected and was already postulated some years ago by the use of other adsorbates.<sup>20</sup> But is certainly interesting to note that also this peculiar aspect of Lewis acidity at the surface of a nominally monophasic oxidic system can be easily evidenced by the adsorption/desorption of 2,6-DMP.

The high acidic strength of the sites responsible for the 8a band at  $\sim 1602 \text{ cm}^{-1}$  on  $\alpha\text{-Al}_2\text{O}_3$  is further confirmed by the persistence of most of the band (now absorbing at  $\sim 1605 \text{ cm}^{-1}$ ) after 2,6-DMP evacuation at 423 K (see curve 2''' in Figure 3).

**2,6-DMP Adsorption onto Sulfated  $\gamma\text{-Al}_2\text{O}_3$ .** The presence of sulfate groups at the surface of oxidic systems is known to modify their intrinsic Lewis acidic properties (e.g., see ref 21). In general terms, the overall Lewis acidity should decrease (as part of the surface is occupied by thermally stable sulfate groups and, thus, a lower amount of cus surface cations can be produced upon activation), and the residual Lewis acidity has been sometimes observed to increase in strength (due to inductive effects from the charge-withdrawing sulfate groups). Moreover, surface sulfates most often induce Brønsted (protonic) acidity, as indicated by the adsorption of strong bases like, for instance, ammonia or pyridine, which can form surface ammonium or pyridinium ions, respectively.<sup>22,23</sup>

Surface sulfate species on oxidic systems are characterized by typical vibrational modes located at  $\nu < 1500 \text{ cm}^{-1}$ .<sup>23</sup> The spectral features of these modes depend on the hydration/dehydration degree achieved by the sample, and in this respect,  $\gamma\text{-AS}$  makes no exception. On passage from a highly hydrated system (curve 1 in Figure 4a) to a more dehydrated one (curve 2 in Figure 4a), the spectral profile of surface sulfates evolve from a typical narrow three-band spectrum (ionic sulfates, similar to mono- and bidentate sulfato complexes<sup>24</sup>) to a well-separated two-band spectrum (typical of highly covalent multibridged sulfates<sup>25</sup>), with a high- $\nu$  component at  $\sim 1380 \text{ cm}^{-1}$  (the S=O stretching) and a complex low- $\nu$  envelope at  $\nu < 1200 \text{ cm}^{-1}$  (the S–O stretching range). The dotted-line traces in Figure 4a represent the spectral profile of the corresponding pure  $\gamma$ -alumina, vacuum activated in the same conditions.

If we carry out 2,6-DMP adsorption onto  $\gamma\text{-AS}$  activated in vacuo at 573 K (see Figure 4b, curve 2'), several bands forms in the 1700–1500  $\text{cm}^{-1}$  spectral range, as detailed in the following. There is a broad three-band profile at  $\nu < 1610 \text{ cm}^{-1}$ , with peaks evident at  $\sim 1602$ ,  $\sim 1595$ , and  $\sim 1580 \text{ cm}^{-1}$ , and an additional two-band envelope located at  $\nu > 1620 \text{ cm}^{-1}$ , with broad peaks evident at  $\sim 1650$  and  $\sim 1630 \text{ cm}^{-1}$ . On the basis of existing literature data on the adsorption of 2,6-DMP, the latter bands can be ascribed to the 8a, 8b vibrational modes ( $\sim 1650$  and  $\sim 1630 \text{ cm}^{-1}$ ,

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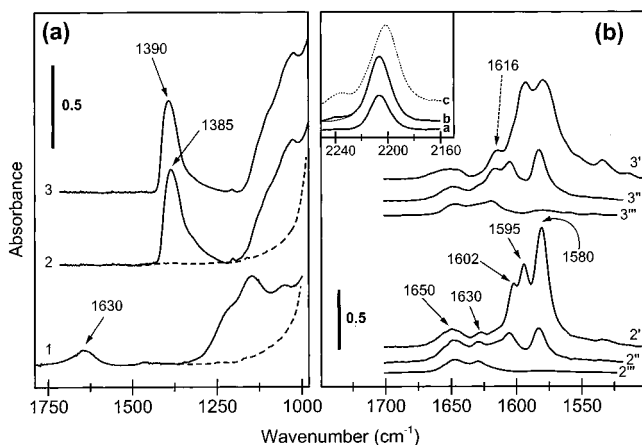
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**Figure 4.** (a) IR spectra in the 1800–900  $\text{cm}^{-1}$  region ( $\nu_{\text{S=O}}$  and  $\nu_{\text{S-O}}$  modes of surface sulfates) of a  $\gamma$ -AS sample activated in vacuo for 1 h at BT (curve 1), 573 K (curve 2), and 773 K (curve 3). The dashed traces represent the spectral profile of the corresponding unsulfated  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> samples. (b) Spectral features in the analytical range of the 8a, 8b modes (1700–1500  $\text{cm}^{-1}$ ) of 2,6-DMP adsorbed onto  $\gamma$ -AS activated in vacuo at 573 K (spectral set 2) and at 773 K (spectral set 3). The curves marked with the prime symbol refer to 2,6-DMP adsorption at BT and under a relatively high pressure ( $\sim 4$  Torr), whereas the curves marked with the double- and triple-primed symbols refer to 2,6-DMP desorption at BT and at 423 K, respectively. The inset presents, for comparison, the spectra of 100 Torr CO adsorbed at BT onto  $\gamma$ -AS activated in vacuo at 573 K (curve a) and 773 K (curve b) and onto a plain  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> sample activated in vacuo at 773 K (curve c).

respectively) of protonated 2,6-DMP species (2,6-DMPH<sup>+</sup>). Protonated species are typically formed in systems carrying a Brønsted acidity, and their presence indicates that, as in many other oxidic systems (e.g., see ref 26), also on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> the presence of strongly acidic surface anions induced the formation of a protonic acidity, which is promptly revealed by the adsorption of 2,6-DMP.

After evacuation of the excess 2,6-DMP at BT (curve 2'' of Figure 4b), the spectral profile remains unchanged at  $\nu > 1620$   $\text{cm}^{-1}$  (meaning that the Brønsted-bound species are strongly adsorbed), whereas at  $\nu < 1620$   $\text{cm}^{-1}$  only one 8a band remains at  $\sim 1604$   $\text{cm}^{-1}$ , together with a residual fraction of the 8b band at 1580  $\text{cm}^{-1}$ . This suggests that the process of sulfation may have brought about the selective screening (by sulfate groups) of the cationic surface terminations that, upon dehydration, lead to the formation of the strongest Lewis acid sites (whose complexes with 2,6-DMP yield the 8a band at  $\sim 1616$ –1618  $\text{cm}^{-1}$ ). But certainly not all of the Al<sup>IV</sup> surface cationic terminations were screened by sulfates, as the medium-strength Lewis acid sites, ascribed to bridging coordinative vacancies, still remain and yield the 8a band at  $\sim 1604$   $\text{cm}^{-1}$ .

If the desorption of 2,6-DMP is carried out at 423 K (see curve 2''' in Figure 4b), only the two bands at  $\nu > 1620$   $\text{cm}^{-1}$  remain with virtually unchanged intensity (the lutidinium surface species are so deduced to be very strongly held), whereas no spectral components remain at lower frequency, meaning that all Lewis-coordinated 2,6-DMP species are desorbed during this mild thermal treatment.

To check if the sulfation process eliminated entirely the cationic sites capable of yielding the strongest Lewis acid sites, the sample  $\gamma$ -AS was activated at a higher temperature (773 K). The spectral profile 3 in Figure 4a

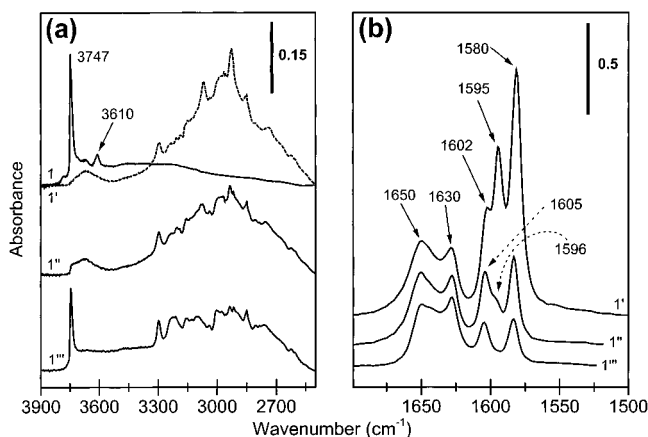
shows that, at this temperature, the concentration and nature of surface sulfates did not change (in fact, surface sulfates are stable up to  $\sim 900$  K), while the surface dehydration proceeded (not shown). The spectral set 3 in Figure 4b indicates that, further to activation at high temperature, an appreciable amount of the Lewis-bound 2,6-DMP species absorbing at  $\sim 1616$   $\text{cm}^{-1}$  formed, although with an intensity definitely lower than that exhibited in the case of a plain  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> sample treated in similar conditions (dealt with in Figure 2). This trend is confirmed by the adsorption of CO at BT and presented for comparison in the inset to Figure 4b: the strongest Lewis complex of CO with *cus* Al<sup>IV</sup> sites, which absorbs on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> at  $\sim 2240$   $\text{cm}^{-1}$ ,<sup>17</sup> does not form on  $\gamma$ -AS activated at 573 K (spectrum a) and forms weakly on  $\gamma$ -AS activated at 773 K (spectrum b), but the intensity is far lower than that produced on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> activated at the same temperature (broken-line spectrum c).

The 8a mode of the strongest Lewis 2,6-DMP complex, absorbing at 1616–1618  $\text{cm}^{-1}$ , remains with a somewhat decreased intensity also after evacuation at 423 K (see curve 3''' of Figure 4b). In all stages of the adsorption/desorption process, the  $\sim 1618$   $\text{cm}^{-1}$  band overlaps severely the low- $\nu$  mode (centered at  $\sim 1630$   $\text{cm}^{-1}$ ) of the Brønsted-bound 2,6-DMP species. Still, the evolution of the spectral profile in set 3 of Figure 4b leaves no doubts on the fact that the  $\sim 1618$   $\text{cm}^{-1}$  band is due to a strong Lewis-coordinated 2,6-DMP species and not to a weak Brønsted-bound 2,6-DMP species. Moreover, these data confirm that, also in the presence of strong Brønsted acid centers, 2,6-DMP adsorption/desorption at temperatures up to 423 K can sample at least the strongest fraction of Lewis acidic sites.

**2,6-DMP Adsorption onto  $\beta$ -Zeolite.** The last system to be examined by the adsorption/desorption of 2,6-DMP is the sample termed H- $\beta$ , i.e. a sample of  $\beta$ -zeolite in its H-form (all cations have been exchanged for H ions). This system is of interest in the present study because of the following: (i) It possesses an abundant natural protonic acidity, deriving from the presence of abundant bridging OH species (typical of zeolitic systems). (ii) It is characterized by large channels ( $5.7 \times 7.5$  Å), so that 2,6-DMP molecules should not be prevented from coming into contact with sites located in all possible positions of the zeolitic structure. (iii) No cations are left within the zeolitic structure. (iv) When treated in vacuo at medium-high temperatures, some of the framework Al atoms (that in zeolites possess the tetrahedral coordination) may dehydroxylate and, thus, originate coordinative vacancies acting as Lewis acid centers. The nature of the latter can now be suitably investigated by the adsorption of 2,6-DMP, in the light of what already observed with the various alumina systems dealt with in previous sections.

Section a of Figure 5 reports the 3900–2600  $\text{cm}^{-1}$  spectral range of H- $\beta$  activated at 873 K. Before adsorption, the complex OH spectral pattern (curve 1) contains several components, among which are clearly evident a strong sharp peak at 3747  $\text{cm}^{-1}$ , due to abundant terminal silanols, and a broad peak at  $\sim 3610$   $\text{cm}^{-1}$ , due to bridging OH species. A minor component at  $\sim 3670$   $\text{cm}^{-1}$  is also present and is normally ascribed to OH groups bound to quasi-extraframework Al<sup>3+</sup> ions.<sup>15</sup> Upon 2,6-DMP uptake (curve 1'), the two major OH components become perturbed by H-bonding ( $\Delta\nu_{\text{OH}} \approx -700$  to  $-800$   $\text{cm}^{-1}$ ), and a very complex pattern appears in the 3300–2650  $\text{cm}^{-1}$  region, mainly due to the  $\nu_{\text{C-H}}$  vibrations of the various 2,6-DMP adsorbed species. (Note that this pattern is far more complex than that observed in the case of 2,6-DMP adsorbed on SiO<sub>2</sub> (Figure 1), as in the latter case only

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**Figure 5.** (a) 3900–2500  $\text{cm}^{-1}$  spectral range (analytical of  $\nu_{\text{OH}}$  and  $\nu_{\text{CH}}$  modes) of a  $\beta$ -H zeolite activated in vacuo at 873 K (curve 1), after the adsorption of a high pressure of 2,6-DMP ( $\sim 4$  Torr; curve 1') and after 2,6-DMP evacuation at BT (curve 1'') and at 423 K (curve 1'''). (b) Spectral features in the analytical range of the 8a, 8b modes (1700–1500  $\text{cm}^{-1}$ ) of 2,6-DMP adsorbed onto  $\beta$ -H activated in vacuo at 873 K. The curve marked with the prime symbol refers to 2,6-DMP adsorption at BT and under a relatively high pressure ( $\sim 4$  Torr), whereas the curves marked with the double- and triple-primed symbol refer to 2,6-DMP desorption at BT and at 423 K, respectively.

liquid-like and H-bonded 2,6-DMP species were formed, whereas here at least one additional Brønsted-bound species is expected to be present.) Upon 2,6-DMP evacuation at BT (curve 1''), the starting OH pattern is only very marginally restored, and this is not so unexpected as also with pure  $\text{SiO}_2$  it was observed (see Figure 1) that the H-bonding interaction between 2,6-DMP and silanols is only partially reversible at beam temperature. 2,6-DMP evacuation at 423 K (curve 1''' of Figure 5a) gives back only  $\sim 2/3$  of the silanol band at 3747  $\text{cm}^{-1}$  (meaning that other forms of silanol perturbation must be present besides the plain ( $\text{N}\cdots\text{H}-\text{O}$ ) H-bonding) and none of the bridging OH band at  $\sim 3610$   $\text{cm}^{-1}$ .

Section b of Figure 5 reports the effects of 2,6-DMP adsorption/desorption in the spectral range of the 8a, 8b modes. There is a very strong doublet of bands at  $\sim 1650$  and  $\sim 1630$   $\text{cm}^{-1}$ , due to the abundant formation of lutidinium species. The intensity of these bands does not change further to 2,6-DMP evacuation at up to 423 K and so explains why the band of bridging OH groups at  $\sim 3610$   $\text{cm}^{-1}$  (responsible for Brønsted acidity) is not restored at all upon evacuation.

In the spectral range below 1620  $\text{cm}^{-1}$ , the adsorption of 2,6-DMP brings about the formation of a strong three-band envelope that, on the basis of what observed in the case of the 2,6-DMP/ $\text{SiO}_2$  system, could be assigned as follows: The band at  $\sim 1580$   $\text{cm}^{-1}$  is the 8b mode, common to all physisorbed and coordinated species, the band at  $\sim 1595$   $\text{cm}^{-1}$  is the 8a mode of physisorbed (liquid-like) 2,6-DMP, and the band at  $\sim 1602$   $\text{cm}^{-1}$  is the 8a mode of 2,6-DMP H-bonded to surface silanols. This assignment, though certainly correct, is not sufficient, and other adsorbed species must be present and contribute to the 8a, 8b envelope. In fact, the following can be stated: (i) After evacuation at BT (see curve 1'' of Figure 5b), a weak but clearly visible component remains at  $\sim 1596$   $\text{cm}^{-1}$  (besides a dominant band at  $\sim 1605$   $\text{cm}^{-1}$ ) that could be ascribed to a fraction of physisorbed 2,6-DMP resisting evacuation at  $\sim 340$  K, as suggested by one of the reviewers of this article. On the basis of what is discussed in the sections dedicated to the 2,6-DMP/Alumina systems, it seems more logical to ascribe the residual 8a band at  $\sim 1596$

$\text{cm}^{-1}$  in curve 1'' (and thus part of the strong component at  $\sim 1595$   $\text{cm}^{-1}$  in curve 1') to the coordination of 2,6-DMP to Al ions carrying an incomplete octahedral coordination ( $\text{Al}^{\text{IV}}_{\text{CUS}}$ ). (ii) After evacuation at 423 K (see curve 1''' of Figure 5b), an appreciable fraction of an 8a band at  $\sim 1605$   $\text{cm}^{-1}$  remains that cannot be ascribed to a fraction of merely H-bonded 2,6-DMP resisting evacuation at  $T > \text{BT}$ . On the basis of what is discussed in the sections dedicated to the 2,6-DMP/Alumina systems, it seems logical to ascribe the residual 8a band at  $\sim 1605$   $\text{cm}^{-1}$  in curve 1''' (and thus part of the band centered at  $\sim 1602$   $\text{cm}^{-1}$  in curve 1') to 2,6-DMP coordinated to bridging coordinative vacancies (for instance,  $\text{Al}^{\text{IV}}-\text{Al}^{\text{VI}}$  pairs, as observed in all transition aluminas and at the surface of  $\alpha\text{-Al}_2\text{O}_3$ ). The persistence, after evacuation at 423 K, of appreciable amounts of Lewis-coordinated 2,6-DMP species justifies the incomplete recovery of the silanol band at  $\sim 3747$   $\text{cm}^{-1}$ , as it is known that terminal OH species at the surface of oxidic systems often interact by H-bonding with the  $\pi$  cloud of Lewis coordinated aromatic heterocyclic bases.

The adsorption of 2,6-DMP on  $\beta$ -H never leads to the appearance of a band at  $\sim 1618$   $\text{cm}^{-1}$ , as also observed with other zeolitic systems. Since, on the basis of what is discussed above, there is no doubt that, when present, the 2,6-DMP band at  $\sim 1618$   $\text{cm}^{-1}$  is due to a strong Lewis coordination, the absence of this band on all zeolitic systems means that, on zeolites, the thermal dehydroxylation of Al centers (either in-framework or extraframework ones) never leads to the formation of the highly uncoordinated  $\text{Al}^{\text{IV}}_{\text{CUS}}$  sites, typical of the highly acidic (spinel) transition aluminas.

## Conclusions

With reference to the 2-fold aim of the present work proposed in the Introduction section, the following can be concluded:

(i) The assignment of a band sometimes observed at  $\sim 1618$   $\text{cm}^{-1}$  upon adsorption of 2,6-DMP on oxidic systems is no longer controversial. The band is due to the 8a ring mode of 2,6-DMP Lewis coordinated to  $\text{Al}^{\text{IV}}$  centers carrying a coordinative vacancy. To the best of our knowledge, this is the highest frequency observed for the 8a mode of a Lewis coordinated 2,6-DMP species, and this fact is not unexpected, as  $\text{Al}^{\text{IV}}_{\text{CUS}}$  yields the highest upward spectral shift also with other Lewis bases (e.g., pyridine uptake at BT on  $\text{Al}^{\text{IV}}_{\text{CUS}}$  presents the 8a mode at frequencies as high as  $\sim 1625$   $\text{cm}^{-1}$ , CO adsorption at BT on  $\text{Al}^{\text{IV}}_{\text{CUS}}$  presents the  $\nu_{\text{CO}}$  mode at frequencies as high as  $\sim 2242$   $\text{cm}^{-1}$ , and acetonitrile- $d_3$  adsorption at BT on  $\text{Al}^{\text{IV}}_{\text{CUS}}$  presents the  $\nu_{\text{CN}}$  mode at frequencies as high as  $\sim 2330$   $\text{cm}^{-1}$ ). The very strong Lewis acid sites yielding, on adsorption of 2,6-DMP, the 8a ring mode at  $\sim 1618$   $\text{cm}^{-1}$  are typical of aluminas with a spinel structure (transition aluminas). All other Al-containing oxidic systems do not present an 8a mode of adsorbed 2,6-DMP at  $\sim 1618$   $\text{cm}^{-1}$ , even if they may possess coordinative vacancies involving either tetrahedral Al centers (zeolites) or quasi-tetrahedral Al centers (defective  $\alpha\text{-Al}_2\text{O}_3$ ).

(ii) The adsorption of 2,6-DMP is a very valuable probe for Brønsted (i.e., protonic) acidic sites. In fact, unlike pyridine (actually, the most commonly used probe) that yields, in its pyridinium form, a weak and broad 19b analytical mode at  $\sim 1550$   $\text{cm}^{-1}$ , 2,6-DMP adsorbed in its lutidinium form yields two strong and well-recognizable 8a, 8b bands centered at  $\sim 1650$  and  $\sim 1630$   $\text{cm}^{-1}$ , respectively. Moreover, surface lutidinium species are very strongly held and remain adsorbed also when all, or most,



of all other 2,6-DMP adsorbed species have been desorbed upon evacuation. But, unlike what is reported in some literature works, 2,6-DMP uptake turns out to be a suitable probe also for Lewis acid centers. If the adsorption is carried out at BT and, possibly, under a reasonably high pressure, all types of coordinated and/or H-bonded species can be differentiated, on the basis of the relevant 8a modes. If 2,6-DMP is evacuated (or the adsorption is carried out under very low pressure), the various coordinated species can be differentiated, on the basis of the persistence of the relevant 8a modes. In particular, if the evacuation is carried out at  $\sim 423$  K (or the adsorption is carried out at

$\sim 423$  K), only the strongest fraction of the strongest Lewis acid sites can still be probed. But in none of the various systems here examined did we observe (as sometimes reported in the literature) that, at temperatures as high as 423 K, steric hindrance prevents 2,6-DMP molecules from being adsorbed at Lewis acid centers, so that only Brønsted acidity (if present) can be probed.

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